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EXCITED STATE KINETICS OF MERCURY AND CADMIUM HALIDES AND NITROGEN FLUORIDE

D. W. Setser

Kansas State University
Department of Chemistry
Manhattan, KS 66506

September 1991

Final Report

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MONTHLY REPORTS FROM KANSAS STATE UNIVERSITY
TO U. S. AIR FORCE

Air Force Weapons Lab

Kirtland Air Force Base, NM

EXCITED STATE KINETICS OF MERCURY AND CADMIUM HALIDES AND NITROGEN FLUORIDE

Contract No: F29601-84-0030

Principal Investigator: D. W. Setser
Department of Chemistry
Kansas State University
Manhattan, KS 66506

Scientific Program Officer: Dr. Vernon Schlie

Contract Duration: March 15, 1984 - March 14, 1985

Monthly Progress Report (First Report)

Report Period: March 15 - April 15 (1984)

Progress Report (1)

The contract award date was March 15, 1984. However, the paperwork giving permission to start formal spending on the contract was not received and approved by Kansas State University until ∿April 2. Thus, the efforts of one postdoctoral fellow and one student were transferred to the Air Force Contract as of April 1.

Two small scale flowing-afterglow systems were in operation at the time the contract was awarded. Therefore, experimental work could be started immediately. The first projects were to measure some quenching rate constants for NF(b) and to demonstrate the general utility of a flowing-afterglow source for NF(b) for both afterglow systems. The NF(b) source is the reaction of $Ar(^3P_{0,2})$ metastable atoms with NF_2. The following total quenching rate constants have been measured for NF(b, v=0) with Air Force support.

Reagent	Rate Constants (10^{-14} cm^3 $molec^{-1}$ sec^{-1})	
O_2	4.2 ± 0.1	
Cl_2	7200 ± 1200	
HF	96.7 ± 15	96.7 ± 15
NF_2	0.6 ± 0.4	
N_2F_4	1.4 ± 0.5	

In the absence of reagent and with ∿ 2 torr of Ar carrier gas pressure, the decay of NF(b) in our system is largely determined by the purely radiative decay rate, i.e., the quenching rate of NF(b) at the Pyrex glass walls is slow (but observable).

During the next month kinetic studies of NF(b) will continue and we will modify the larger flowing-afterglow apparatus for a study of vibrational-to-electronic energy transfer between HF(v) and NF(a).

D. W. Setser

*PS. On my final contract I noted that cadmium had evolved to calcium in the title of the contract. Please check to see that your listing of our contract is correct. I do not want calcium kinetics showing on your computer print-out of our contract title.

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Contract Duration: March 15, 1984 - March 14, 1985

Monthly Progress Report (Second Report)

Report Period: April 15 - March 15 (1984).

Progress Report 2

This monthly period was one of minor experimental activity because the student, Daimay Lin, was writing her Master's Thesis and because the postdoctoral fellow, Dr. Singh, accepted a permanent position and left KSU. The new postdoctoral person arrived (and started work) on May 14. Thus, work has begun on rebuilding the $O_2(a)$, $O_2(b)$ apparatus for the $NF(a) + HF(v)$ experiment. Daimay did the final flow calibrations on her NF(b) apparatus this month and has refined the rate constants for NF(b) quenching. Next month's report will contain a listing of all those rate constants. In general there seems to be a close parallel between the trends in NF(b) quenching rate constants and those for $O_2(b)$.

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Monthly Progress Report (~~Second~~ third Report)

Report Period: May 15 - June 15 (1984).

Progress Report 3 (May 15 - June 15)

A new student, Andy Slagle, and a new postdoctoral fellow, Dr. Habadas, arrived and started work on the contract. Mr. Slagle will continue the HF(b) quenching measurements and Dr. Habadas will do the NF(a) + HF(v) experiments. Mr. Slagle has learned the techniques and added a few rate constants to our listing (attached) of NF(b) quenching, rate constants. During the next two months he will study NF(b) with halogens. Dr. Habadas rebuilt the O_2(a,b) apparatus so that NF(a) + HF(v) could be studied. The building phase is nearly completed and preliminary experiments will be done during late June. Since this work is difficult and since Dr. Habadas is learning techniques, approximately two more months are expected before reliable data can be obtained.

During the June 15 - Sept. 15 period, Setser will be in Grenoble France studying N_2(A) + CdX_2 (X = Br,I) excitation transfer reactions. Dr. Y. C. Yu will be at KSU during this period and he will be handling phone calls, reports etc. Dr. Yu also will supervise Mr. Slagle in the NF(b) + halogen quenching studies. If any formal administrative action on this contract is required, Dr. Copeland, assistant Dept. Head, should be contacted.

Comparison of Rate Constants at 300K (in units of $10^{-14} cm^3 molec^{-1} sec^{-1}$) for the Quenching of $NF(b^1\Sigma^+)$ and $O_2(b^1\Sigma_g^+)$

Q	$k_Q^{NF(b)}$	$k_Q^{O_2(b)}$
HCl	30.2 ± 1.9[a]	4 ± 2[d]
		7.3 ± 0.2[e]
		6.7 ± 3.5[f]
HF	96.7 ± 15[a]	110 ± 20[d]
	100[b]	
CH_4	22.1 ± 1[a]	7.5[f]
CH_3F	20.7 ± 0.3[a]	
CH_3Cl	23.6 ± 2.3[a]	80 ± 40[d]
CH_3Br	17.9 ± 0.8[a]	
CH_3I	35.9 ± 4.2[a]	
CH_2Br_2	25.9[a]	
$CHCl_3$	6.4 ± 1.7[a]	
CHF_3	63.5[a]	
CF_3NO	11.6 ± 1.2[a]	
CF_3Br	1.20 ± 0.18[a]	
NH_3	8.91 ± 0.18[a]	200[f]
		130 ± 20[d]
CO_2	0.53 ± 0.41[a]	30 ± 10[d]
O_2	3.8 ± 0.1[a]	0.01[g]
CO	1.50 ± 1.23[a]	0.33[g]
Cl_2	7020 ± 1130[a]	
Br_2	11830 ± 839[a]	
NF_2	0.5 ± 0.4[a]	
N_2F_4	0.4 ± 0.1[a]	
NF_3	180 ± 70[c]	
Ar	<0.001[c]	
H	300[b]	

a. This work.

b. M. A. Kwok, J.M. Herbelin and N. Cohen, Electronic Transition Lasers, p. 8, 2nd Ed., The MIT Press, 1975.

c. P. H. Tennyson, A. Fintijn and M. A. A. Clyne, Chem. Phys., 62, 171, 1981.

d. J. P. Singh and D. W. Setser, J. Phys. Chem., to be published.

e. R. G. O. Thomas and B. A. Thrush, Proc. Roy. soc. A, 287, 350, 1977.

f. M. J. E. Gunthjer and D. R. Snelling, J. Photochem., 4, 27, 1975.

g. F. Stuhl and K. H. Welge, Can. J. Chem., 47, 1870, 1969.

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Contract Duration: March 15, 1984 - March 14, 1985

Monthly Progress Report (Fourth Report)

Report Period: June 15 - July 15 (1984)

Progress Report 4

The student, Daimay Lin, who was working on this project, finished her M.S. degree and a new student, Andy Slgale, is able to run her apparatus after a couple weeks' training. Andy is currently extending Daimay's measurements on NF(b) quenching to other interesting molecules.

The initial testing on the NF(a) + HF(v) experiment has been successful. Qualitative work by Dr. Jan Habdas shows that HF(v) + NF(a) $\rightarrow$ NF(b) is observed. An emission spectrum of NF(a), NF(b) and possibly HF(v) is attached to this report. The monochromator calibration is in progress. This is essential before doing any quantitative measurements. Also computer simulations of the kinetic equations are being carried out.

Telephone conversation w Dr Habdas 25 JUL 84
Spectrum attatched is that produced by the reaction

can obtain yellow nitrogen emission by increasing NF_2

$$NF_2 + H \rightarrow NF(a) + HF(v) \rightarrow ?$$

$N_2F_4 \xrightarrow{heat} NF_2$

H from microwave discharge

Ar buffer gas ~1 Torr
quenches emission at higher pressures

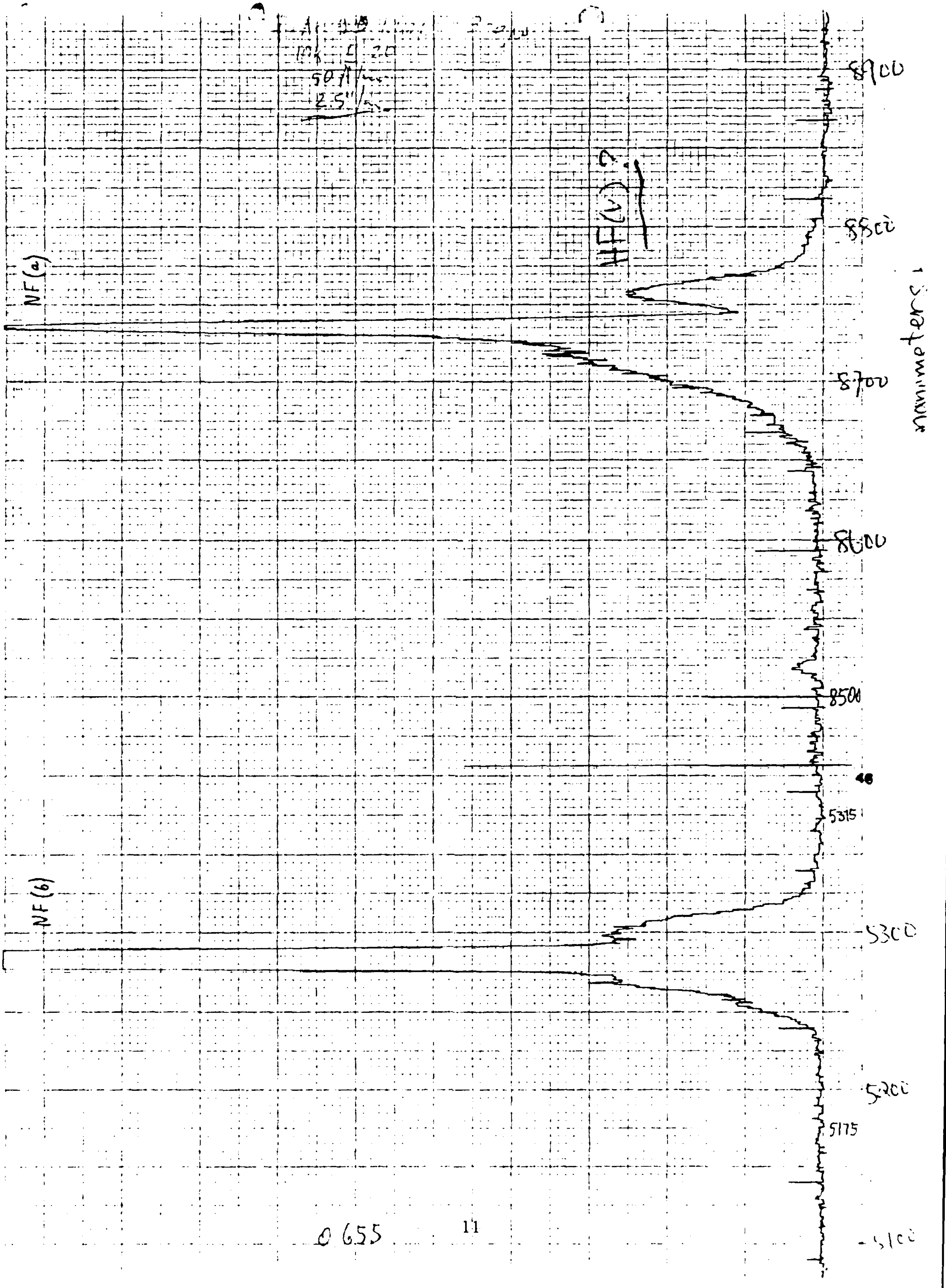
Next step is direct production of HF by

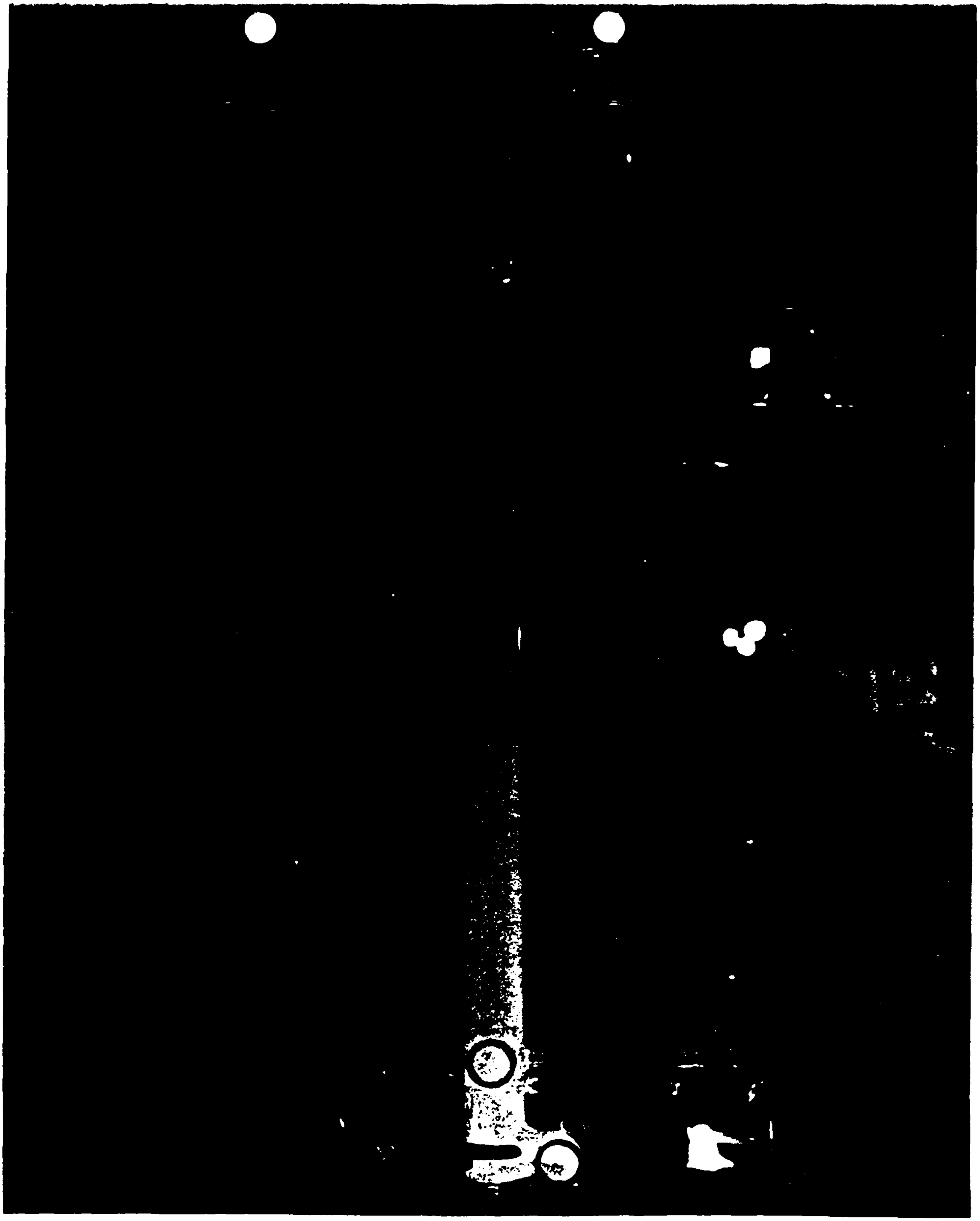
$$F + H \rightarrow HF(v)$$

$CF_4 \xrightarrow{microwave} F$

$H_2? \xrightarrow{microwave} H$

will allow separation of HF(v) emission feature


NF(a)
NF(b)
HF(v)?
8900
8800
8700
8600
8500
5315
5300
5200
5175
nanometers
0655



NF(b) afterglow

$Ar^* + NF_3 \longrightarrow NF(b)$

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Contract Duration: March 15, 1984 - March 14, 1985

Monthly Progress Report (Fifth Report)

Report Period: July 15 - August 15 (1984)

Progress Report 5

In collaborative work at Grenoble Dr. Setser has demonstrated that the $CdI_2 + N_2(A)$ reaction gives $CdI(B) + I$ with a branching fraction of ~ 0.1 and a total quenching rate constant of $\sim 4.3 \times 10^{-10}$ cm^3 $molecule^{-1} s^{-1}$.

V-E transfer from HF(v) to NF(a) was observed. The preliminary experiments indicated about 30% increase in NF(b)/NF(a) ratio upon the addition of HF(v) to the $H + NF_2$ system. Quantitative measurements are in progress.

The spectrum attached to last report was obtained under these conditions:

Total Ar flow	2.8×10^{-3} mole/s
Total reactor pressure	0.76 torr
Pumping speed	~ 82 m/s
H_2 flow	2.4×10^{-6} mole/s
NF_2 flow	1.7×10^{-6} mole/s
Slits	400 μm
Scan rate	50 Å/min

Experiments on the E-E transfer between NF(b) and halogens or interhalogens are also being carried out by Mr. Slagle and Dr. Y. C. Yu. A pre-reactor has been constructed to generate IF(X), etc.

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Contract Duration: March 15, 1984 - March 14, 1985

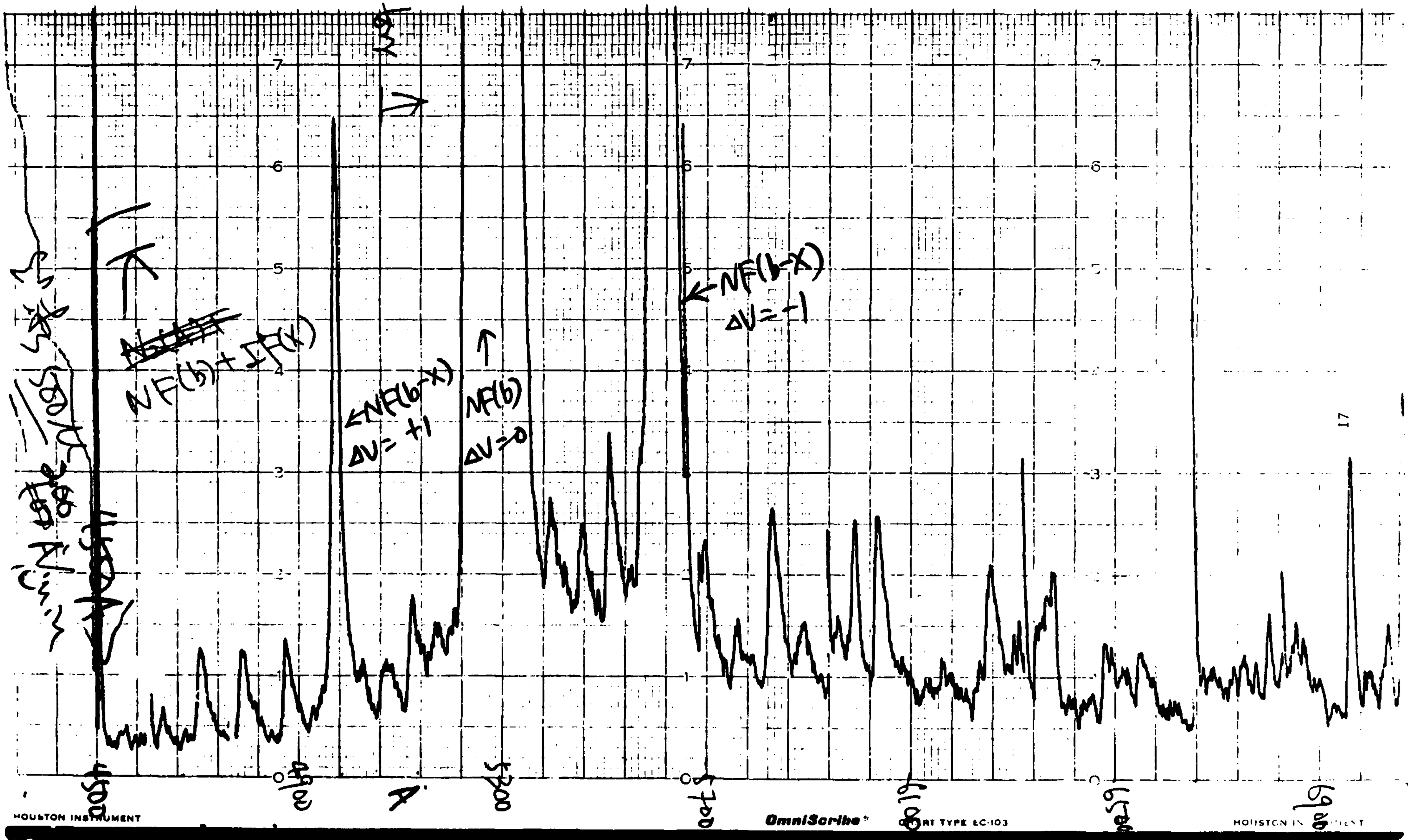
Monthly Progress Report (Sixth Report)

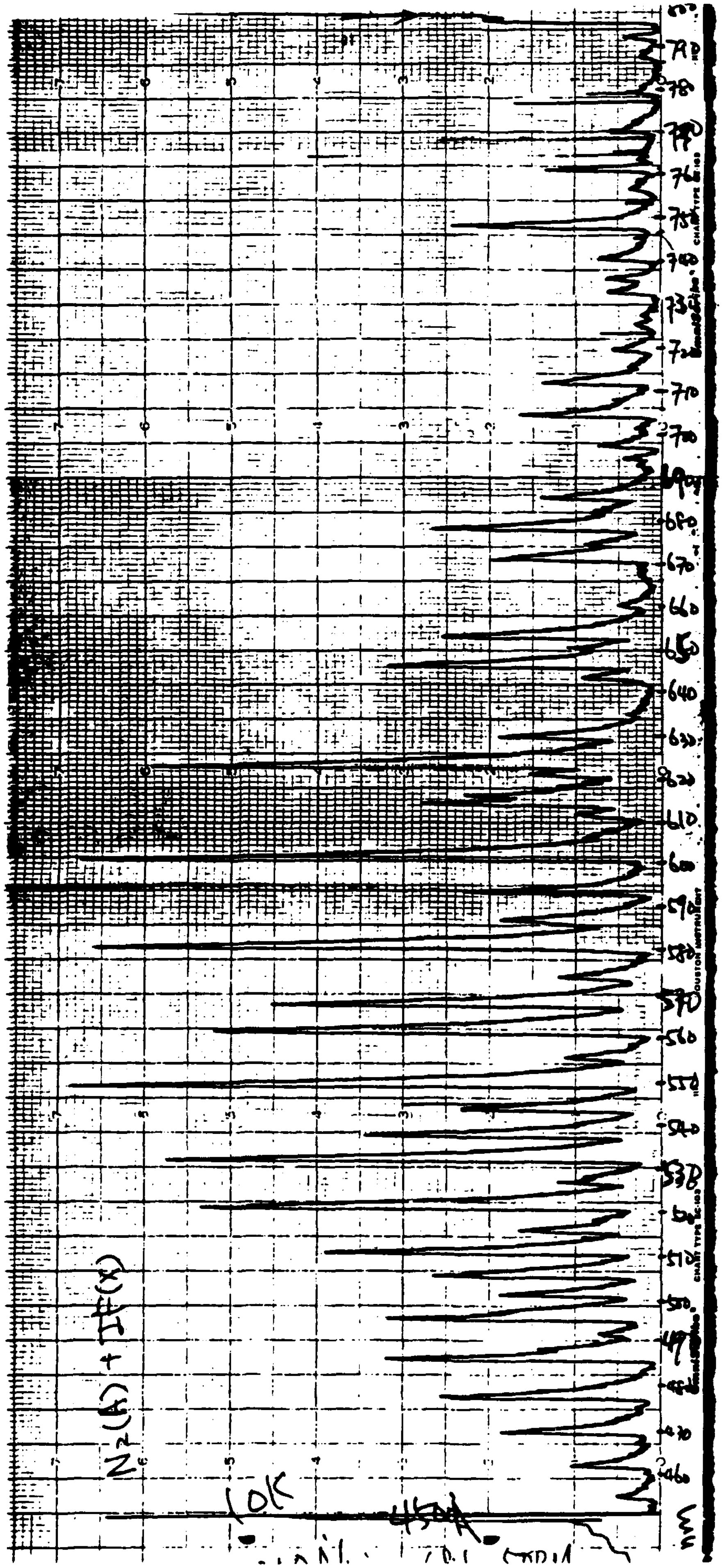
Report Period: August 15 - September 15 (1984)

The pre-reactor for in situ synthesis of unstable interhalogens works well for IF(X). E-E transfer from both NF(b) and $N_2(A)$ to IF(X) has been observed by Dr. Y. C. Yu. IF(B-X) emission spectrum from $NF(b) + IF(X) \longrightarrow NF(X) + IF(B)$ and $N_2(A) + IF(X) \longrightarrow N_2(X) + IF(B)$ are attached. Other E-E transfer reactions observed are summarized below:

$$NF(b) + I_2(X) \rightarrow I_2(B,v' \leq 29) + NF(X)$$
$$N_2(A) + I_2(X) \rightarrow I_2(D') + N_2(X)$$
$$N_2(A) + IBr(X) \rightarrow IBr(D') + N_2(X)$$

No emission can be found for NF(b) + Cl_2, Br_2, ICl, IBr and $N_2(A)$ + Cl_2, Br_2, ICl. For $N_2(A)$ + BrF(X) reaction, definite conclusion can not be made since it is not sure that BrF(X) is generated by the pre-reactor from F + Br_2.


4500
4900
Å
5300
5700
6100
6500
6900
$\leftarrow$ NF(b-X) $\Delta v = -1$
$\leftarrow$ NF(b-X) $\Delta v = +1$
NF(b) $\Delta v = 0$
NF(b) + IF(X)
17
HOUSTON INSTRUMENT
OmniScribe
CHART TYPE EC-103



N2(A) + IF(X)
10K
450A
460
470
510
550
560
580
590
600
610
640
650
660
670
680
700
710
750
760
780

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Contract Duration: March 15, 1984 - March 14, 1985

Monthly Progress Report (Seventh Report)

Report Period: Sept. 15 - Oct. 15 (1984)

Professor Setser returned from France Sept. 20 and Dr. Yu returned to Taiwan the next day. During this report period, no significant experiments have been done because we are waiting on arrival of N_2F_4 (we have been promised some tanks from Aerospace and a small gift from Hercules). This should be enough for the critical experiments. During this period, we have designed and built second generation flow reactors which should enable the critical experiments to be done for characterizing the following two reactions.

i) $NF(a) + HF(2) \rightarrow NF(b) + HF(0)$

ii) $NF(b) + IF \rightarrow NF(X) + IF(B)$

Dr. Yu's last report (#6) was a bit too brief. Indeed, transfer from NF(b) to IF was observed; however, the IF(B) intensity was very low and there may have been traces of $N_2(A)$ in the NF(b) flow system. Thus, we have no firm information about the NF(b) + IF reaction. With good fortune, we may have conclusive results in another month.

During Setser's stay in Grenoble, the $N_2(A)$ reactions with all the Cd and Zn halides were examined. The best system seems to be CdI_2. The CdI_2 total quenching rate constant was $4.3 \pm 1.5 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} and the branching fraction for CdI(B) formation was 0.08. All the other compounds had similar total quenching rate constants, but even smaller branching fractions for excited state product formation. Thus, dissociative excitation transfer from $N_2(A)$ with the Hg, Cd, and Zn halides do not have sufficiently large branching fractions for HgX(B), CdX(B) or ZnX(B) to be very interesting as laser systems. We plan to do some spectroscopic interpretations of the ZnX(B-X) and CdX(B-X) spectra from $N_2(A)$ excitation and write a paper in collaboration with the Grenoble laboratory. However, this is not a high priority item and work will not begin until summer of 1985.

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Contract Duration: March 15, 1984 - March 14, 1985

Monthly Progress Report (Eighth Report)

Report Period: October 15 - November 15 (1984)

Progress Report #8

During this report period, we have installed the improved flow reactors that will allow the two following reactions to be characterized.

(i) NF(a) + HF(v) → NF(b) + HF(v-2)

(ii) NF(b) + IF → NF(X) + IF(B)

We have received a N_2F_4 tank from Aerospace Corporation and we are expecting additional tanks of N_2F_4 from Hercules Corporation and from the Air Force Weapons Laboratory. We have received CF_3I from the Air Force Laboratory and we have found a commercial source of C_2F_5I. These are used to prepare IF from F atom reactions. Thus, all chemicals finally are available for the experiments.

During this report period, Dr. Habadas explored the F + $H-N_3$ reaction as an alternative soruce for NF(a) for study of reaction(i).

(iii-a) F + $H-N_3$ → HF(v) + N_3

(iii-b) F + N_3 → NF(a) + N_2

This NF(b) source, if fact, appears to be <u>superior</u> to the H + NF_2 reaction for our purposes. In particular, there appears to be less complication from secondary reactions because excess F with NF(a) causes fewer difficulties than H with NF(a). Based upon our preliminary work, we plan to use reactions (iii) to generate NF(b) for study of reaction (i) and we will not need to use N_2F_4 (NF_2 + H) to generate NF(a). From our qualitative observation,we believe that reaction (iii-b) must have a rate constant larger than the 2×10^{-12} cm^3 $molecule^{-1}$ s^{-1} value quoted in the literature. After finishing with reaction (i) we would like to study (iii).

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Scientific Program Office: Dr. Vernon Schlie

Contract Duration: March 15, 1984 - March 14, 1985

Monthly Progress Report (Tenth Report)

Report Period: December 15, 1984 - January 15, 1985

Progress Report # 10

We have continued our experiments to characterize the following two reactions.

$$\text{(i)} \quad NF(a) + HF(v) \xrightarrow{k_v} NF(b) + HF(v-2)$$

$$\text{(ii)} \quad NF(b) + IF \xrightarrow{k_B} NF(X) + IF(B)$$

Some progress has been made in each case.

The disk-drive for the data system of the FT-IR was returned and new calibrations for the FT-IR system were done last week. Thus, we are ready to observe HF(v) and HF(v-2) via infrared emission from (i). The kinetic modeling studies mentioned in the last report were continued, and we confirmed our suspicion that HF(v=0) from the NF(a) source reaction (either $F + HN_3$ or $H + NF_2$) was causing kinetic complications because of the quenching of NF(b) by HF(0). Thus, we are trying to develop a NF(a) source that is free of HF(0). We are exploring the $F + Cl\text{-}N_3$ reaction. The preparation line for ClN_3 has been built and will soon be tested. If this reaction proves to be a source for NF(a), we believe that the assignment of k_v from (i) will be more reliable because the reverse reaction will be less important.

We began the study of (ii) by training the graduate student operator. Stable halogen molecules were selected for investigation. To my surprise the work proved not to be routine and a mistake was discovered in our earlier quenching measurements (by Ms. Lin) for Cl_2 and Br_2. Those rate constant values, which were included in previous reports and in a preprint, are too large by factors of 2-3. The correct values are

$$k_{Cl_2} = 1.8 \pm 0.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_{Br_2} = 6.0 \pm 1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_{ICl} = 1.0 \pm 0.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

As reported by Dr. Yu in the work done in the summer, these reactions do not give observable Cl_2^*, Br_2^*, or ICl^* emission. These rate constants have been measured several times and the results are reproducible. Apparently Ms. Lin made a mistake when she prepared the Cl_2 and Br_2 mixtures with Ar in her preliminary investigation of Cl_2 and Br_2. The rate constants for the other reagents reported in the preprint were measured with pure gases and those rate constants are satisfactory. We now are ready to test our method for generating IF and to measure the room temperature quenching rate constant and branching fraction for IF(B) formation. We are conserving N_2F_4 to ensure that we can do the IF experiments. However, we also are proceeding in a conservative step by step fashion to make sure that errors are avoided (or at least identified) in handling the halogens.

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Monthly Progress Report (Eleventh Report)

Report Period: January 15, 1985 - February 15, 1985

Progress Report # 11

We have continued our experiments to characterize the following two reactions:

$$\text{(i)}\quad NF(a) + HF(v) \xrightarrow{k_v^b} NF(b) + HF(v\text{-}2)$$

$$\text{(ii)}\quad NF(b) + IF \xrightarrow{k_B} NF(X) + IF(B)$$

$$\rightarrow \text{other channels}$$

Some progress has been made in each case.

The attempt to develop a NF(a) source that was free of HF(0) for study of reaction (i) failed. The F + $Cl\text{-}N_3$ reaction does not cleanly give FCl and N_3, rather the first step seems to be addition to $Cl\text{-}N_3$ with NFCl + N_2 being the products. Thus, we have returned to F + NH_3 as the NF(a) source reaction. We now are collecting data (NF(b) and HF(v) emission intensities) and we will be using these data to assign k_v^b. This project is in the terminal phase and soon will be completed.

We have been testing our method of generating IF for the study of reaction (ii). Preliminary experiments have been done; however, some kinetic difficulties have been discovered. For example, we have found that the microwave discharged Ar/CF_4 mixture gives some quenching of both $N_2(A)$ and NF(b), although pure CF_4 gives no measurable quenching of either. Therefore, we are exploring different sources for F atoms, since the F + CF_3I reaction is used to generate IF. We have observed the rather weak IF(B-X) emission excited by the NF(b) excitation-transfer reaction. Comparison of the NF(b) and IF(B) emission intensities for a known [IF] suggests an excitation rate constant of ~2-5 x 10^{-12} cm^3 $molecule^{-1}$ s^{-1}. tentative Definitive studies can be done to establish this value. Measuring the total quenching rate constant will be more difficult. During the next 4 week period, efforts will be made to obtain quantitative data for the total quenching of (ii), so that a branching reaction for IF(B) formation can be assigned.

me

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Contract Duration: March 15, 1984 - March 14, 1985 (extended to April 1, 1985)

Monthly Progress Report (Twelfth Report)

Report Period: February 15, 1985 - April 1, 1985

Progress Report # 12

We have continued our experiments to characterize the following two reactions:

$$\text{(i)} \quad NF(a) + HF(v) \xrightarrow{k_v^b} NF(b) + HF(v-2)$$

$$\text{(ii)} \quad NF(b) + IF \xrightarrow{k_B} NF(X) + IF(B)$$

$$\rightarrow \text{other channels}$$

Some progress has been made for each case.

We have collected data, NF(b) and HF(v) emission intensities, using F + C_2H_6 as the HF(v) source and F + HN_3 as the NF(a) source for reaction (i). The major experimental effort this month has been development of a method to measure [F] and to more fully characterize the NF(a) source reaction. We have used these data to assign $k_{v=2}^b$ as ~ 0.5×10^{-11} cm^3 $molecule^{-1}$ s^{-1}. We plan to choose another fuel, probably SiH_4, and generate mainly HF(v=3) so that $k_{v=3}^b$ can be assigned. This project is in the terminal phase and soon will be completed.

The IF(B) excitation and the NF(b) total quenching rate constants have been measured at room temperature using the F + CF_3I reaction to generate IF(X). Comparison of the NF(b) and IF(B) emission intensities for a range of known [IF] given an excitation rate constant of $1.5 \pm 0.5 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. The total quenching rate constant for an equal molar mixture of IF(X) and CF_3 was measured by observing the decay of NF(b) in the flow reactor as a function time and [IF]. The total quenching rate constant was $1.1 \pm 0.4 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}. This rate constant pertains to an equal concentration of IF and CF_3, but IF is expected to dominate the quenching.

We now are in the process of preparing the final report on this contract, which terminated on April 1, 1985. The two week extension from March 15 to April 1 was granted by the Chicago Monitoring Office for administrative reasons.